

SCIENCE FOR CERAMIC PRODUCTION

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CERAMIC FACING TILES BASED ON LOCAL POLYMINERAL CLAYS

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It is demonstrated that after polymineral clays from the Republic of Tatarstan are treated by various methods improving the quality of clay materials (diluting mixture with activated water, treating mixture in an electric classifier, introducing technological additives, such as mechanoactivated quartz-glaucanite sand or phosphoric and high-melting clay) can be used in semidry molding combined with slip preparation of molding powder to produce tiles for interior and exterior facing satisfying standard requirements.

The production of ceramic tiles requires high-quality refractory and high-melting clays. However, the reserves of these materials in Russia are limited and it is necessary to search for new nontraditional resources and industrial waste. The problem of producing competitive product can be solved as well by improving the quality of natural clays using state-of-the-art concentration equipment and technologies [1].

By way of example, we can describe the research performed at the Central Research Institute of Geology of Non-metal Minerals for the purpose of producing high-quality construction ceramics [2]. Production of ceramic tiles does not exist in the Republic of Tatarstan and setting up such production requires corresponding mineral materials. Local argillaceous materials have poor quality and, therefore, cannot be used for the production of ceramic tiles for exterior and interior facing that would meet the prescribed technological standard (the bending strength of tiles for interior wall decoration should be at least 15 MPa, water absorption not more than 16%; cold resistance of outside facing tiles of thickness 9 mm should be not less than 35 cycles and their water absorption not more than 10%).

To improve the physicomechanical properties of finished product, different methods of treatment of materials were used (electrokinetic dehydration, diluting mixtures with activated water, activation in electric classifier) [2], various molding and firing regimes were tested, and technological additives were introduced into mixtures. The research was performed on clays from the Yuzhno-Chistopol'skoe and Krasnogorskoe deposits in Tatarstan, which represent different mineralogical-technological varieties [3]. The content of

the montmorillonite component in the first variety is 35% and in the second one 28%.

The preparation of clay material was performed in the following way. After natural drying it was crushed in a jaw crusher up to passing through a sieve with 1-mm cell size. The prepared powder was diluted with water to prepare slip of moisture 45–55%, thickening coefficient 2.1, and density 1.45 g/cm³, which was periodically agitated. Next, the mixture was dried in natural conditions and in a drying cabinet (at a temperature not higher than 90°C) with subsequent production of molding powder (particle size below 1 mm, moisture 7–10%).

After the molding powder aged for 24 h, tiles of size 150 × 40 × (7–9) and 125 × 125 × (8–10) mm were molded on a hydraulic press by two-stage bilateral compression. The molding pressure was 25.0–32.5 MPa and the initial pressure (to remove air) was 6.0–8.0 MPa. After drying, the samples were fired at a temperature of 1000–1100°C (temperature rise 100°C per 10 min) with an exposure at the final temperature equal to 15 min.

Table 1 gives data on the effect of various methods for treating argillaceous materials on the physicomechanical characteristics of samples.

The properties of tiles molded from initial Yuzhno-Chistopol'skoe clay do not satisfy the standard requirements. The electrokinetic method used for dehydration of a slip mixture from 50 to 30% moisture does not perceptibly change its parameters. The use of activated water for slip preparation insignificantly improves its physicomechanical parameters.

Good results have been achieved in using clay from the Yuzhno-Chistopol'skoe deposit preliminary treated in an

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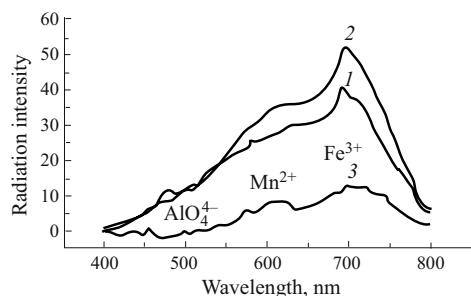


Fig. 1. Spectra of photoluminescence of clay materials: 1) initial; 2) treated; 3) difference spectrum.

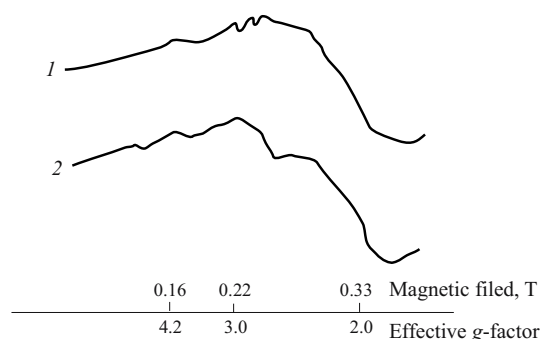


Fig. 2. EPR spectra of initial (1) and treated (2) clay material.

electric classifier. Such treatment activates clay by increasing its active surface as a result of the rupture of numerous bonds in dispersion and disaggregation of clay particles. The granulometric composition of clay changes as well. Highly disperse molding powder has been obtained, in which more than half (65%) of particles are below 63 μm . The plasticity of clay grows as well (from 8.9 to 13.2). Tiles made from such powder have bending strength of 17.0 MPa and water absorption of 7.8%. This indicates that the activation performed facilitates increases the activity of clay particles and sinterability of powder, i.e., give reason to grade this material as standard one.

The treatment of batch consisting of 80% initial clay and 20% high-melting clay in an electric classifier leads to a further increase in the bending strength of samples (up to 22.1 MPa) with a slight increase in water absorption (8.1%).

TABLE 1

Method of treating clay material	Bending strength,* MPa	Water absorption, %
Electrokinetic dehydration	14.1/15.5	10.0/10.9
Thinning mixtures with activated water	14.9/18.5	8.1/8.2
Activation in electric classifier	17.0/15.8	7.8/11.9
Initial material	13.5/14.1	9.9/11.5

* Numbers before slash indicate values for Yuzhno-Chistopol'skoe clay samples, numbers after slash – Krasnogorskoe clay samples.

The increased water absorption may be related to the modification of the pore space structure due to the modification of the granulometric composition of the molding powder.

To clarify the mechanism of defect formation and kinetics of structural transformations of mineral components, we performed combined differential thermal and x-ray quantitative phase analysis, as well as the electron paramagnetic resonance (EPR) and photoluminescence methods.

The thermal analysis curves of the initial and treated clay samples exhibit two intense endothermic effects corresponding to the removal of weakly bonded (adsorbed) water and dehydration related to the removal of structural OH groups. The temperature intervals of the specified transformations and the configuration of thermal analysis curves have insignificant differences, which may point to slight structural modifications caused by electric classification.

X-ray phase analysis identified a slightly higher (by 2%) content of the montmorillonite component in mechanically activated clay. The photoluminescence spectra of activated clay exhibit additional luminescence bands related to Mn^{2+} , Fe^{3+} , and Al^{3+} ions (Fig. 1). The modifications in the curves amount to 20 – 22%.

The EPR spectra of two samples (initial clay and clay after electric classification), despite their general similarity, differ by a shift of some spectral ranges toward higher values of the g-factor (from 3.0 to 3.5), the emergence of new lines, and the growing intensity of the general spectrum of Fe^{3+} ions (Fig. 2).

The same ceramic mixture was used to study the effect of molding pressure (varying from 25.0 to 32.5 MPa). Raising the molding pressure by 7.5 MPa changes the bending strength and water absorption values within a narrow interval (by 3.2 MPa and 1.0%, respectively). Therefore, the molding pressure of 25 – 27 MPa can be regarded as optimum.

Technological additives tested in this study were zeolite-bearing clays of the Bol'she-Aksinskoe manifestation and quartz-glaucanite sand and phosphorites from the Vozhinskoe deposit in the Republic of Tatarstan, which were preliminarily subjected to mechanical activation in a ball mill for 20 min. The use of 20% zeolite-bearing clays or 40% quartz-glaucanite sand and phosphorite did not improve the physicomaterial properties of tiles. The introduction of 20% mechanoactivated quartz-glaucanite sand and phosphorite yielded samples with bending strength 20.0 and 19.7 MPa, water absorption 6.5 and 7.0 %, and shrinkage 3.0 and 2.7%, respectively. In this case the parameters of the samples satisfy the standard requirements.

The optimum quantity of high-melting clay additive from Sukhoi Log (Chelyabinsk Region) is 20%. In this case the compression strength of samples is 17.0 MPa and water absorption 7.5%.

Adding chamotte into ceramic mixtures not only helps to utilize waste, but also decreases fire shrinkage, which decreases deformation in the course of drying and firing. Samples containing 20% high-melting clay and 5% chamotte obtained by grinding a fired material to a fraction below 1 mm

have strength of 17.9 MPa and water absorption of 9.3%. The pretreatment of clay (this particular composition) in an electric classifier leads to a slight decrease in strength (16.2 MPa) and water absorption (8.6%), which is presumably due to the modification of the granulometric composition of the molding powder and the pore space at the moment of the formation of a liquid phase in firing ceramics. When firing is performed at 1100°C, along with increasing strength (up to 21.5 MPa) and decreasing water absorption to a minimum value (5.8%), the fire shrinkage grows to 4.7%. In this case adding chamotte to the ceramic mixture does not lower fire shrinkage, which is equal to 3.3 – 3.6% in all considered variants.

Generalized technological testing have been performed using optimum ceramic mixtures: 80% clay + 20% mechano-activated quartz-glaucanite sand or phosphorite; 80% clay + 20% high-melting clay; 100% clay treated in an electric classifier. It is found that glazed facing tiles for interior and exterior decoration obtained in testing meet the standard requirements with respect to all prescribed parameters.

The tiles were glazed with majolica glazes produced at the Dulevo Paint Factory. We used acid-resistant glazes Nos. 3031, 3094, 3101, and 120. Glazes were prepared in accordance with their application recommendations. The glazes were deposited on prefired tiles and then fired at 1000 – 1030°C with the temperature rise rate equal to 100°C per 10 min and with natural cooling in the furnace. The glazed surface has no crackles, pinholes, or bare spots. The thermal resistance of the glaze is 150°C, hardness by the Mohs scale is 5, the glaze is chemically resistant.

Sample prepared for the initial Krasnogorskoe clay using the slip technology also have unsatisfactory parameters. The dehydration of the slip mixture on an electrokinetic plant from 50 to 30% moisture improves the tile parameters, consequently, they meet the requirements imposed on tiles for interior decoration. Thinning the mixture with activated water raises the bending strength by about 30% and decreases water absorption by 3.3%, which is the optimum result obtained in laboratory technological tests. Treatment of Yuzhno-Chistopol'skoe clay with activated water does not improve the properties of ceramics. This may be due to the fact that some of argillaceous materials (the montmorillonite

component) are naturally “cemented”, accordingly, only the effect of activated water in the state of a slip opens the active surface of particles.

Treating Krasnogorskoe clay in the electric classifier insignificantly improves the properties of tiles (bending strength grows by 12%, water absorption decreases by 0.4%).

The application of quartz-glaucanite and phosphorite from the Vozhinskoe deposit (fraction below 1 mm) as additive had a negative effect. Good parameters have been registered in samples produced from a slip with 20% refractory clay from the Sukhoi Log deposit. The bending strength is 17.6 MPa, water absorption 10.4%, and total shrinkage 1.6%. According to x-ray phase analysis, this ceramics has twice as much wollastonite as the corresponding ceramics from Yuzhno-Chistopol'skoe clay. Tiles from mixtures containing 75% clay, 20% high-melting clay, and 5% chamotte thinned with activated water have bending strength 18.2 MPa and water absorption 9.2%.

The optimum mixtures (80% clay + 20 % high-melting clay and 75% clay + 20% high-melting clays + 5% chamotte) mixed with natural or activated water were used to produce glazed tiles of a larger size (120 × 120 × 8 mm). By their physicomachanical properties and exterior appearance, they meet the standard requirements imposed on tiles for interior decoration and outside wall facing.

The performed studies prove the possibility of producing high-quality glazed ceramic tiles for interior decorating and outside facing from local polymineral clays after their preliminary concentration using different methods.

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